Synthesis and Comparison of the Reactivity of 3,4,5-1*H*-Trinitropyrazole and Its *N*-Methyl Derivative

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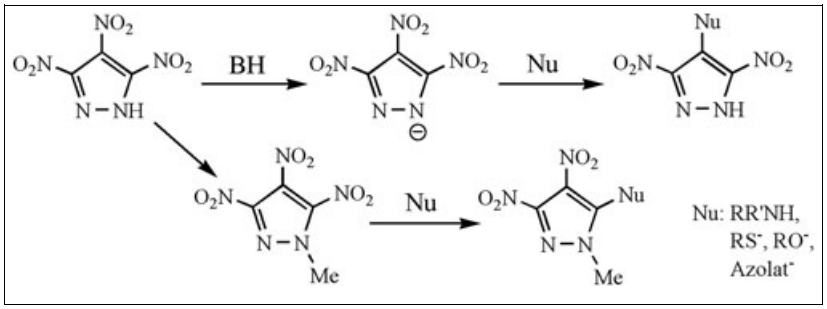

3,4,5-Trinitro-1*H*-pyrazole (**1**) has been obtained *via* nitration of 3,5-dinitropyrazole with mixture of sulfuric and nitric acids. Compound **1** reacts with excess ammonia and aliphatic amines, in the presence of bases with NH-azoles, phenols, thiols, and triflouroethanol at mild conditions in water. All these reactions occur as the nucleophilic substitution of the nitro-group at position 4 in **1** affording 4-R-3,5-dinitropyrazoles. The product of methylation of **1**, *N*-methyl-3,4,5-trinitropyrazole (**4**), also reacts with thiols, phenols, oximes, ammonia, amines, and NH-azoles. The reactions proceed with high yields but nucleophilic substitutions in these cases occur regioselectively at position 5 in **4** to afford 5-R-3,4-dinitropyrazoles.

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INTRODUCTION

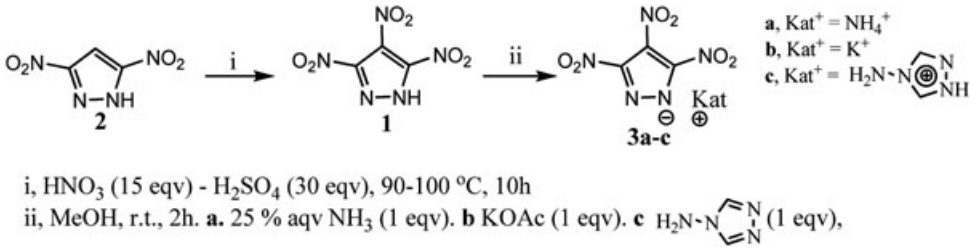
Nitropyrazoles and dinitropyrazoles are widely used in organic synthesis including the synthesis of valuable biologically active compounds. Effective methods of synthesis 3,4-dinitropyirazoles and 3,5-dinitropyirazoles by direct acid nitration, as well as *N*-nitropyrazole N→C rearrangement in combination with detailed methods of a cycle functionalization based on nucleophilic NO_2-group replacement, make this type of pyrazoles exclusively attractive as starting compounds for the synthesis of a wide range of not easily accessible nitropyrazole derivatives [1–4].

In our previous works [5–8], it was shown that 3,4-dinitropyrazoles and 3,5-dinitropyrazoles react with *S*-, *N*-, and *O*-nucleophiles to form product of regiospecific substitution of 3-nitro or 5-nitro group, respectively. The selectivity of substitution was found to depend on the mutual arrangement of the nitro-substituents at the heterocyclic core.

Recently, Herve et al. synthesized *N*-unsubstituted pyrazole which has the nitro groups at all three ring carbon atoms, i.e., 3,4,5-trinitro-1*H*-pyrazole (TNP, **1**) [9]. In this work, TNP was obtained using three approaches: (i) through the oxidation of 4-amino-3,5-dinitropyrazole or 5-amino-3,4-dinitropyrazole by the mixture of 90% H_2O_2 and concentrated sulfuric acid in dichloroethane; (ii) *via* the diazotation of 5-amino-3,4-dinitropyrazole by sodium nitrite in 20% sulfuric acid; (iii) and by the nitration of 3,5-dinitropyrazole with the mixture of sulfuric and nitric acids in 60% oleum. In our independent work, TNP was synthesized by the oxidation of 5-amino-3,4-dinitropyrazole but with the mixture of 84% H_2O_2 in concentrated sulfuric acid [10]. Later, Shreeve et al. obtained TNP *via* the oxidation of 4-amino-3,5-dinitropyrazole with the mixture of 30% H_2O_2 and concentrated sulfuric acid [11]. Because of all these publications, such an interesting object as TNP became available for the researchers.

As a part of our ongoing study on nitropyrazoles, it appeared very interesting to investigate the nucleophilic substitution in TNP. Herve etal. found that under the action of ammonia and alkali TNP could undergo the nucleophilic substitution of 4-nitro group, although they pointed out "the nitro at C4 is therefore strongly linked to the ring so that drastic conditions are required to provoke its displacement" [9]. It is well known, however, that the twist of aromatic nitro group in respect to the appropriate ring (which was established in [9] for the TNP and its anion) accelerates the substitution reaction due to easier formation of the *ipso*-σ-complex between

Scheme 1



i, HNO_3 (15 eqv) - H_2SO_4 (30 eqv), 90-100 °C, 10h
ii, MeOH, r.t., 2h. **a.** 25 % aqv NH_3 (1 eqv). **b** KOAc (1 eqv). **c** H_2N-triazole (1 eqv),

nucleophile and nitro arene. This stage was found to be the rate-determining one in substitution reactions in nitro heterocycles and hexanitrobenzene [12].

To shed a light on the problems mentioned above, the more thorough study on the reactivity of TNP and its simple *N*-methylated analog (1-methyl-3,4,5-trinitropyrazole, MTNP) was initiated. This article summarizes and extends our preliminary results on the nucleophilic substitution in TNP [13,14] and MTNP. In addition to the synthetic part, the article discusses the data of X-ray single crystal studies of key products and intermediates.

RESULTS AND DISCUSSION

The synthesis of TNP, its salts, and MTNP. TNP **1** was synthesized using the nitration of 3,5-dinitropyrazole (**2**) by the mixture of concentrated nitric and sulfuric acids (Scheme 1) [15]. Such a mixture is usually being used forthe transformation of 3(5)-nitropyrazole into 3(5),4-dinitropyrazole [16].

Trinitropyrazole **1** is a strong NH-acid ($pK_{a20°C}$ = 0.05, H_2O, spectrophotometry [17]) being highly soluble in water and many typical organic solvents such as ether, ethylacetate, dioxane, THF, alcohols, acetonitrile, DMF, and DMSO. Such high acidity makes possible the formation of salts of **1** with a wide variety of bases possessing different basicity (see Scheme 1) including such a weak base (pK_{BH+} = 3.23 [18]) as 4-amino-1,2,4-triazole (product **3c**, see Scheme 1) [19].

The structure of TNP **1** and its salt **3c** (Fig. 1) was established by X-ray diffraction analysis (XRD) of their single crystals (*vide infra*).

N-Methyl-3,4,5-trinitropyrazole (MTNP, **4**) was synthesized [20] with 95% yield through the methylation of **1** with dimethylsulfate in the presence of $NaHCO_3$; the very mild conditions of this reaction—20°C, water—should be stressed here (Scheme 2). The structure of **4** was confirmed by XRD (Fig. 2, *vide infra*).

XRD study of TNP, its *N*-aminotriazole salt 3c, MTNP, and ammonium salt of 4-amino-3,5-dinitropyrazole (5a) [21]. In contrast to the crystallographic data reported by Herve [9], trinitropyrazole **1** (Fig. 1) crystallizes with three independent molecules in an asymmetric unit [22]. In all cases, the geometric parameters of the pyrazole ring fall into the ranges typical for this class of compounds and are close to the calculated ones for TNP [23], but the disposition of the nitro groups in respect to the heterocycle ring is significantly different. Thus, the twist angle of the central nitro group in the independent species is 82.5(1)°, 63.8(1)°, and 69.5(1)°. The same value for the moiety N(3) O(1)O(2) is 0.9(1)°, 14.8(1)°, and 9.7(1)°, and that for the third nitro group is 2.7(1)°, 7.5(1)°, and 7.7(1)°, respectively. The salt **3c** exhibits the similar tendency: the

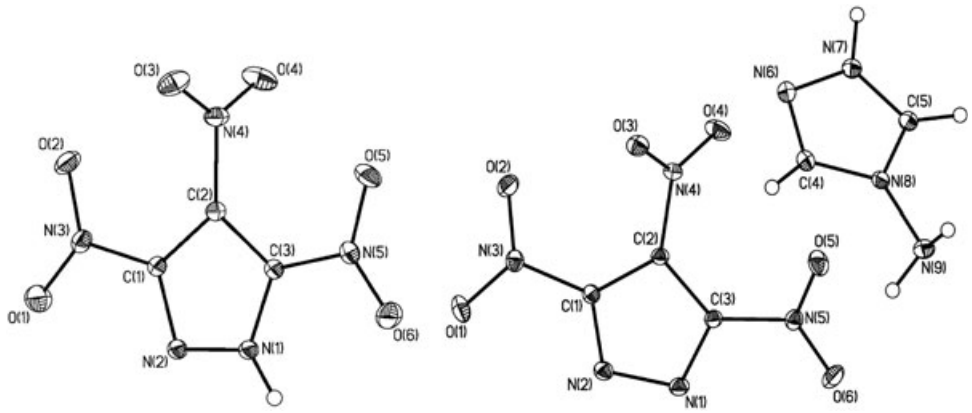
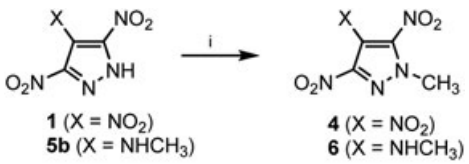


Figure 1 General view of the compound TNP **1** (left) and its salt **3c** (right) in representation of atoms *via* thermal ellipsoids at 50% probability level.

Scheme 2



1 (X = NO_2) **4** (X = NO_2)
5b (X = $NHCH_3$) **6** (X = $NHCH_3$)

i: Me_2SO_4 (1.2 eqv) - $NaHCO_3$ (2 eqv), H_2O, r.t., 7h

corresponding twist angle is 11.5(1)°, 55.5(1)°, and 12.9(1)° in the case of the nitro groups at the atoms C1, C2, and C3.

Apart from the differences in the twist angles of the nitro groups, comparing the TNP **1** and its salt **3c** shows the variation in the geometry of the central cycle. The greatest difference [0.014(2) Å] is observed for the bond N N, which is longer in the case of the salt, apparently, due to the formation of the strong H-bond with its counter ion partner. In a crystal of **1**, each molecule of TNP forms only one H-bond of the intermediate strength; the latter is N(1) H(1)···N(2) between the neighboring independent molecules [N···N 2.967(1)–3.059(1) Å, NHN 161(1)–173(1)°]. In a crystal of **3c**, the cation is involved in the formation of two H-bonds: N(9) H(9NB)···N(1) [N···N 3.064(1) Å, NHN 156(2)°] and N(7) H(7N)···N(2) [N···N 2.788(1) Å, NHN 179(1)°], whose action together lead to the greater perturbation of the TNP moiety than the corresponding H-bonds in **1** do. The resulting H-bonded chains hold together by means of N (9) H(9NA)···N6 H-bond [N···N 3.264(1) Å, NHN 154(2)°] between cations as well as of various contacts between the nitro groups with the distance O···O as small as 2.940(1) Å. The smallest intermolecular O···O distance in **1** is 2.912(1) Å with the independent species being different in a type and a number of interactions they are involved in. The formation of the three-dimensional (3D)-framework in the two crystals is accomplished by numerous O···π (**1** and **3c**) and C H···O (**3c**) contacts.

Taking into account that the twist angle of the central NO_2 group in the sodium salt of TNP is markedly bigger (82°) [9] than that in **3c**, the degree of this twist seems to depend on the nature of a counter ion: in the case of Na^+, which is a rather small cation and cannot be involved (in contrast to **3c**) in the H-bonding with the TNP moiety, the twist of the group 4-NO_2 is more pronounced. One can assume that in solutions of TNP salts, where cations and anions are separated by the solvent molecules, the twist angle for this group is more than 80°; hence, there is no conjugation between the moiety 4-NO_2 and the pyrazole cycle, while it is definitely not the case of the nitro groups 3-NO_2 and 5-NO_2 in both the salt **3c** and that with sodium cation [9] as well as in TNP itself.

The XRD investigation of MTNP **4** (Fig. 2) showed that its molecular geometry (well reproduced in the recent quantum chemical investigation of MTNP [23]) is close to that in TNP **1** and its salt **3**. In particular, the twist angles for the nitro groups are 10.7(1)°, 69.6(1)°, and 10.2(1)°, respectively. The nitro groups also participate in the formation of various intermolecular O···O interactions with the corresponding interatomic separation being as small as 2.917(1) Å. As in the case of the **1** and **3**, a number of contacts of the O···π and C H···O types also contribute to the formation of the 3D-framework.

According to the XRD data (Fig. 3), the substituents in **NH_4-5a** (synthesis *vide infra*) are nearly coplanar with the pyrazole cycle—the trend that was previously observed for the 1H-pyrazole analog and its crystallosolvate with DMSO [24]. Thus, the twist angle for the nitro groups N(3)O_2 and N (5)O_2 in **NH_4-5a** is 3.5(1)° and 1.8(1)°, respectively [4.0(1)° and 8.8(1)° in the case of the second independent moiety], while for NH_2 it is equal to 4.0(1)° and 4.6(1)°. Such a disposition is, apparently, ensured by the intramolecular interactions—the hydrogen bonds N(4) H(4NA)···O(5) and N(4) H(4NB)···O(2) [N···O 2.836(1)–2.850(1) Å, NHO 118 (1)–122(1)°]. The groups NH_2 also participate in formation of intermolecular H-bonds N(4) H(4NA)···O(5A) [N···O 2.934(1)–3.027(1) Å, NHO 156(1)–161(1)°], which assemble the independent anions into dimers. The latter are involved in the H-bonds with cations [N···N 2.889(1)–2.933 (1) Å, NHN 166(1)–179(2)°; N···O 2.960(1)–3.044(1) Å, NHO 125(1)–157(1)°] and water molecules [N···O 3.100 (1)–3.128(1) Å, NHO 139(1)–153(2)°; O···O 3.000(1)–3.213 (1) Å, OHO 138(1)–153(1)°] leading to the formation of the H-bonded 3D-network. The latter is completed by the interactions between the nitro groups; the smallest O···O distance being 2.941(1) Å.

Nucleophilic substitution in TNP. On studying the reactivity of **1**, we have found that TNP exhibits unusual behavior in the reactions with nucleophiles. It readily (water, room temperature) reacts with an excess of ammonia [25] and aliphatic amines to form products **5a**–**h**, which result from the regiospecific substitution of a nitro group at position 4 in starting TNP (Scheme 3). The full

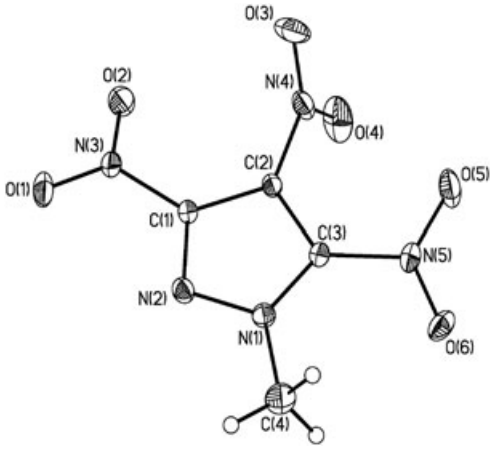


Figure 2 General view of MTNP **4** in representation of atoms *via* thermal ellipsoids at 50% probability level.

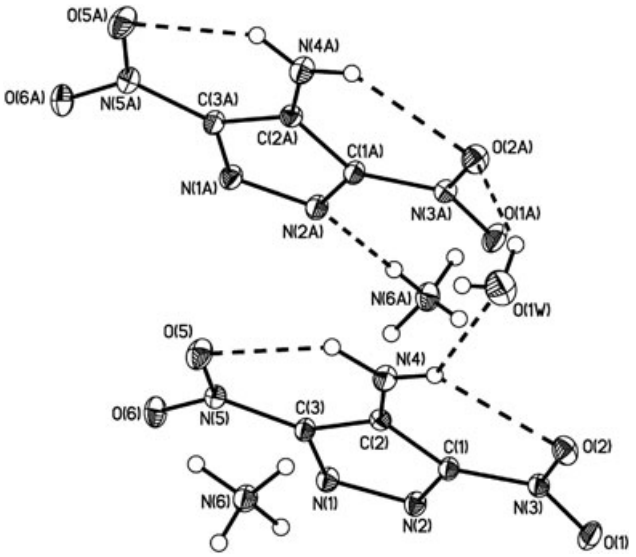


Figure 3 General view of the salt **NH_4-5a** in representation of atoms *via* thermal ellipsoids at 50% probability level.

conversion of TNP was observed after 10 h of reaction, and this was visualized by the precipitation of red solid which proved to be (alkyl)ammonium salt of 4-NR′R″-dinitropyrazole from initially homogeneous solution [26]. The following treating of the intermediate salt with 20% H_2SO_4 furnishes the final 4-substituted 3,5-dinitro-1*H*-pyrazoles **5a**–**h** (see Scheme 3).

The formation of **5a** [4,27] was confirmed by the XRD study of the semi hydrate of its ammonium salt **NH_4-5a** (see Fig. 3). The additional prove came from the independent synthesis of **5a** *via* the alkaline hydrolysis of carbamate **7** [28] (Scheme 4).

In the same manner as with amines, in the presence of inorganic bases, TNP reacts with phenols, triflouroethanol, and thiols to form 4-substituted 3,5-dinitro-1*H*-pyrazoles **8** and **9** (see Scheme 3). The reactions proceed in water at room temperature in the presence of two equivalents of NaOH, which means that TNP reacts with R*O*- and R*S*-anions in its own anionic form. The phenols with strong electron-withdrawing groups such nitro or cyano group do not react with TNP at all under these conditions. In the case of *O*-nucleophiles, the full conversion is achieved after 10 h. It should be noted that TNP itself is easily hydrolyzed even in the presence of $NaHCO_3$ [29] forming disodium salt **10** (see Scheme 2).

Independently on their nature, the thiols react with TNP considerably faster them *O*-nucleophiles, and the reactions accomplish in 3 h. The products **8a**–**f** and **9a**–**f** were formed as simply isolable solids after acidifying the reaction mixture by 20% H_2SO_4.

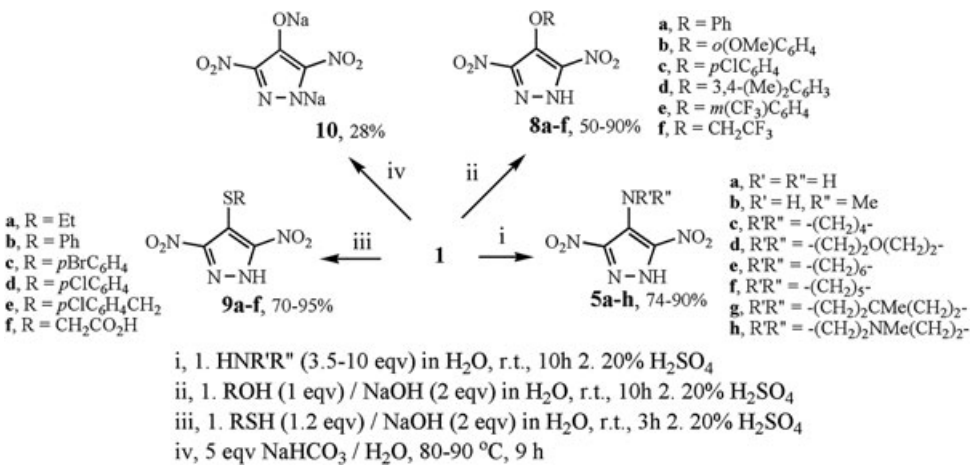
Such an easy course of TNP substitution reactions with various heteroatom nucleophiles stimulated us to study reactivity of **1** toward *N*H-azoles capable to ionize N H bond, fully or partially, in water under the action of NaOH.

We have found that TNP indeed reacts with various nitropyrazoles, 2-methyl-4-nitroimidazole, and 1,2,4-triazole in water in the presence of two equivalents of NaOH. All these reactions also represent the nucleophilic substitution of a nitro group at position 4 in TNP nucleus affording the previously unknown 3,5-dinitro-4-(*N*-azolyl)pyrazoles **11a**–**f** (Scheme 5).

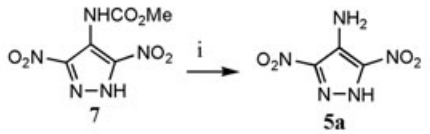
Unlike the case of the discussed above reactions of TNP with aliphatic amines and anionic *O*- and *S*-nucleophiles, the reactions with azoles require 9 hours of heating at 80–90°C for completion.

At the same conditions, the *N*H-azoles having p*K*a less than 9, such as 4-nitro-5(3)-carboxamidopyrazole, 3(5),4-dinitropyrazole and 3-nitro-1,2,4-triazole do not react with TNP. Despite these results, the reaction of TNP with azoles could be regarded as an efficient synthetic procedure, complementary to the known synthetic approaches to the

Scheme 3



Scheme 4



i: KOH (3 eqv) / H_2O, 80-90 °C, 7h 2. 20% H_2SO_4

4-(*N*-azolyl)pyrazoles [30]. 4-(*N*-Azolyl)pyrazoles themselves represent an important class of compounds due to their diverse biological activity [31] as well as due to their potential as the polydentate ligands in Pd-catalyzed amination reactions [32].

Therefore, the easy nucleophilic substitution of 4-NO_2-group in pyrazole family has been established for the first time based on reactivity study of the wide range of compounds. It was only known that the substitution in 1-R-3,4-dinitropyrazoles with various nucleophiles occurs exclusively at the position 3. The products of substitution at position 4 have never been documented even in trace amounts despite the activating nature of 3-NO_2 group [3,5]. Another important noting is that the interaction of nucleophiles with TNP is virtually the interaction with its anion which is readily formed at the reaction conditions (two equivalents of alkali). Thus, such an easy nucleophilic substitution occurring in the anionic form of TNP looks hardly possible at the first glance. Hence, the reactions of TNP open new synthetic challenges in the pyrazole chemistry through functionalization of position 4 *via* nucleophilic substitution in TNP anion.

Nucleophilic substitution in MTNP. From the XRD data on TNP **1**, its salt **3c**, and MTNP **4** (*vide supra*) it is clearly seen that the main structural feature in all the molecules is the pronounced tilting of 4-NO_2 group in respect to the plane of the pyrazole core. This points out to the low degree of conjugation (if any) between the aromatic heterocyclic ring and this substituent. In the case of TNP itself, such a feature has a pronounced effect on the reactivity toward the nucleophiles—the unusual substitution occurs at the position 4 even in theanionic form of **1**. Having this result in mind, it was quite challenging to study the reactivity of MTNP in the reactions with various *S*-, *N*-, and *O*-nucleophiles.

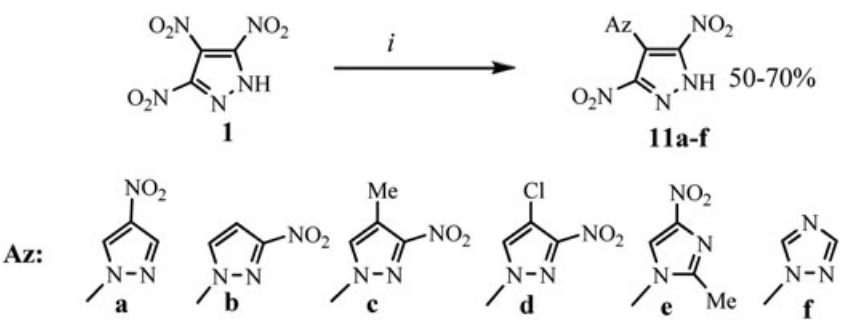
We have found that with all aforementioned nucleophiles MTNP behaves completely different compared to TNP: in all the cases, the nucleophilic substitution of a nitro group takes place regiospecifically at the position 5.

The list of *N*-nucleophiles chosen for the study of MTNP reactivity includes ammonia, aliphatic primary and secondary amines, aromatic and heteroaromatic amines, hydrazide, and *N*H-azoles (Scheme 6). The reactions were carried out in methanol at room temperature using two equivalents of the appropriate nucleophile. Under these conditions, the products **12** were isolated in 60–90% yields, and the full conversion of the starting compounds was achieved after 2 h for the case of amines. For the completion of the reactions with *N*H-azoles, much longer time was required, in some cases up to 48 h. This fact could be explained by the very low basicity of the reagents (pK_{BH+} for alkylpyrazoles 3.04–2.48; for 2-methyl-4-nitroimidazole, 0.86; for 1,2,4-triazole, 2.45) [18]. The azole-containing products **13** are formed in 60–80% yields.

The least basic nitropyrazoles used in our experiments (pK_{BH}^{+} for 4-nitropyrazole, 2.0; for 3-nitropyrazole, 4.66 [18]) did not react with MTNP without addition of a base assisting the transformation of a reagent into its more nucleophilic anionic form (pK_a of nitropyrazoles ~9.6–9.8 [18]). Thus, the reactions of MTNP with nitropyrazoles in the presence of one equivalent of NaOH in aqueous acetonitrile accomplish in one hour affording the products **14a**,**b** in 80–90% yield (Scheme 6).

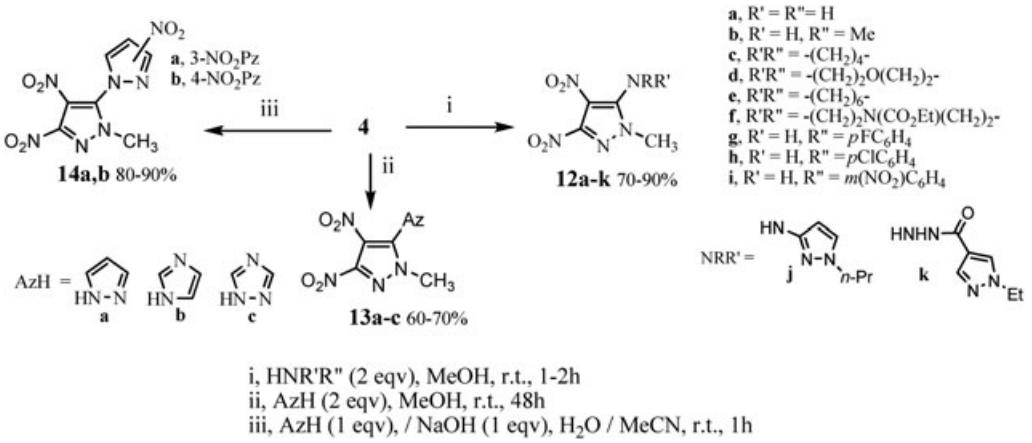
The anionic forms of *O*- and *S*-nucleophiles react with MTNP much easier than that of *N*-nucleophiles (Scheme 7). Phenols, among them those containing one and two nitro groups, as well as propargyl alcohol and oximes in the presence of 1 equiv of NaOH were used as *O*-nucleophiles in

Scheme 5



i 1. AzH (1 eqv) / NaOH (2 eqv), H_2O, 80-90°C, 9h 2. 20% H_2SO_4

Scheme 6



i, HNR'R" (2 eqv), MeOH, r.t., 1-2h
ii, AzH (2 eqv), MeOH, r.t., 48h
iii, AzH (1 eqv), / NaOH (1 eqv), H_2O / MeCN, r.t., 1h

our experiments. The reactions were carried out in aqueous acetonitrile at room temperature, under these conditions the full conversions were achieved in 1 h, and the yields of products **15**, **16**, and **17** were about 66–85%.

Being the most reactive among used by us, heteroatomic anionic nucleophiles, *S*-nucleophiles, react with MTNP at room temperature very quickly—the reactions accomplish in 15 min giving the products **18** yields up to 95%. In the case of ethanethiol, the reaction even needed the external cooling.

Therefore, compounds **12–18** are the products of regioselective nucleophilic substitution of a nitro group at position 5 of the pyrazole unit.

Then we have found that one of the remaining in **12** nitro groups, i.e., 3-NO_2, could also be substituted (Scheme 8). Several example reactions have also shown that dinitropyrazoles **12** react selectively with nucleophiles to produce the products of 3-NO_2 substitution. These data are in agreement with our previous results [5]. But such a process needs much more drastic conditions—the reflux for 12 h with an excess of the amine in methanol. These reaction sequence—double nucleophilic substitution of 5-NO_2 and then 3-NO_2—opens a synthetic route to unsymmetrical 3,5-diamino-4-nitropyrazoles **19**.

NMR Studies of the synthesized compounds. The structures of all the products of TNP substitution reactions (**5a–h**, **8a–f**, **9a–f**, **10**, and **11a–f**) were confirmed by ^{13}C-NMR spectroscopy with the help of the reference signals of compound **5a** whose structure was unequivocally established by XRD and by synthetic transformation of **7** (*vide supra*). For the correct assignment of carbon signal, the rules well known for nitropyrazoles has been applied—the consequence of chemical shift is in the row C3≥C5>C4 [2,3]—together with quadrupole broadening of the signal of carbons bound to NO_2 groups on ^{14}N nuclei.

Because of the fast *N*H-exchange process, in all ^{13}C-NMR spectra of the products of TNP substitution reactions are seen only two signals of carbon atoms of the pyrazole core, i.e., C4 and C3,5. This tells us about symmetrical structure of all products.

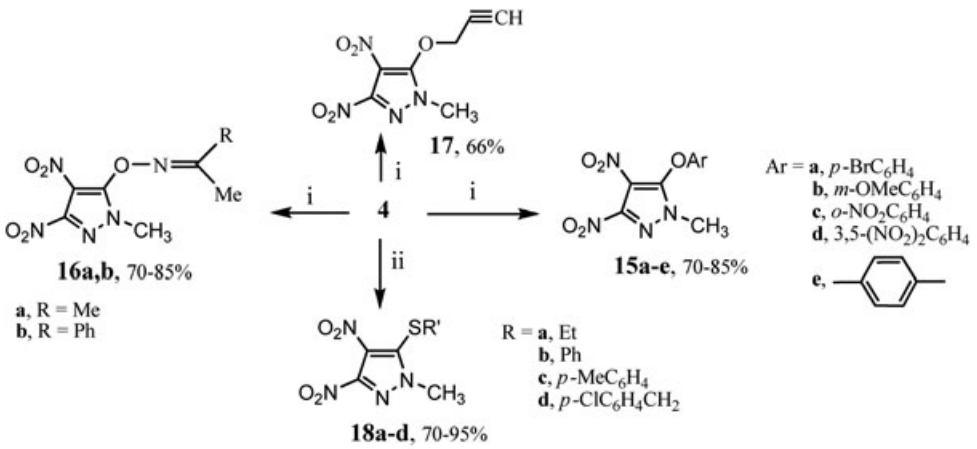
The additional proves of the products structures come from the NMR study of compound **6** which is the product of **5b** *N*-methylation (Scheme 2). Two dimensional correlation spectroscopy NMR HMBC allows one to recognize the long-range spin-coupling constant ^{1}H–^{13}C between $\underline{NH}CH_3$ proton and carbon atoms C3 (δ 140.80 ppm) and C5 (δ 133.82 ppm). These data together with chemical shift of carbon atom adjacent to the $NHCH_3$ fragment (δ 130.87 ppm) and with the absence of the spin–spin interactions between $NHCH_3$ and N1 CH_3 (NOESY data) clearly show that the fragment $NHCH_3$ in the product **5b** is located at position 4 of the pyrazole ring.

The structures of the all the products of MTNP substitution reactions **12–18** were established on the bases of their ^{13}C-NMR spectra as well as by the comparison of them to ^{13}C-NMR spectra of products **5**, **8**, **9**, and **11**. For the detailed assignments of the signals, the same rules as for spectra of **5**, **8**, **9**, and **11** were applied.

The characteristic feature of ^{1}H-NMR spectra of the products **12–18** is the position of *N*-Me signal, δ 3.60–4.00, compared to isomeric 4-substituted *N*-methyl-3,5-dinitropyrazoles where the signals have δ ≥ 4.15 ppm (see lit. [8,13,32]). Moreover, the additional characteristic parameter in the spectra of **12–18** is the existence of high-field signal C4–NO_2 as well as two low-field signals assigned to C3 and C5, one of them (C3–NO_2) being broadened.

The additional prove of the structure **12b** which is the isomer of the product **6** was made using two-dimensional NMR techniques HMBC and NOESY. In HMBS spectrum, the long-range ^{1}H–^{13}C spin coupling for C5 (δ 147.50 ppm) is observed not only for the group $NHC\underline{H}_3$ but also for the protons of the fragment N1–$C\underline{H}_3$. Moreover, the NOESY experiment shows the interaction of $NHC\underline{H}_3$ protons with those of N1–$C\underline{H}_3$ group. This is possible only in the case

Scheme 7



when $NHCH_3$ group is positioned at the position 5 of the pyrazole ring (Fig. 4).

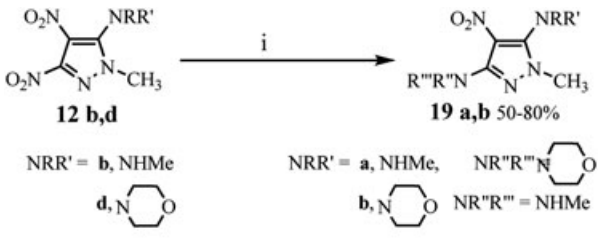
The features of nucleophilic substitution reactions in TNP and MTNP. The above-described unusual reactivity of TNP needs the explanation. The mild conditions of the reactions —generally, room temperature, water—that are not typical for the aromatic nucleophilic substitution also require the comment. At the first glance, the reasonable explanation of the substitution of 4-NO_2 group in TNP is the presence of two adjacent electron-withdrawing nitro groups at positions 3 and 5 of the pyrazole ring which enhance the reactivity of the internal NO_2. If so, one should expect the same 4-NO_2 substitution also in MTNP. However, our experiments clearly show that in this case, the only leaving group is the NO_2 at position 5, and 4-NO_2 does not take any part in the reaction.

This behavior of MTNP follows the course of reactions found recently in our lab: in the case of N-substituted 4-Z-1-R-3,5-dinitropyrazoles, the nucleophiles substitute only 5-NO_2 group independent on the nature of 4-Z and 1-R substituents [6–8]. Such a result was confirmed by quantum chemical calculations which explains the difference in activation energies by the difference in positive charges at positions 3 and 5 [6].

Without detailed structural data on molecules of TNP and MTNP, the reasonable explanation of the difference in their reactivity toward the same nucleophiles could be the difference in the degree of conjugation of 4-NO_2 group with the pyrazole nucleus. However, XRD data discussed above unequivocally and data Herve [9] show that in TNP, in its salts, and in MTNP, the plane of the 4-NO_2 group is tilted significantly, and the dihedral angles are nearly the same for three different molecules. This means that in all the cases, the conjugation between 4-NO_2 and pyrazole ring is neglectable. At the same time, two other nitro substituents (3-NO_2 and 5-NO_2) lie almost in the plane of the central core.

All these data allow us to conclude that the reason for the unusual substitution of 4-NO_2 group in TNP should be related to the anionic form of TNP in those reactions. It is commonly accepted that the nucleophilic substitution in N-anions of nitropyrazoles is not possible [7]. It is well-accepted knowledge, that the position 4 in pyrazoles is considered as "electrophilic" and positions 3 and 5 as "nucleophilic." This governs the electrophilic nitration on position 4, and nucleophilic substitution on positions 3 and 5 [1,6–8].

Scheme 8



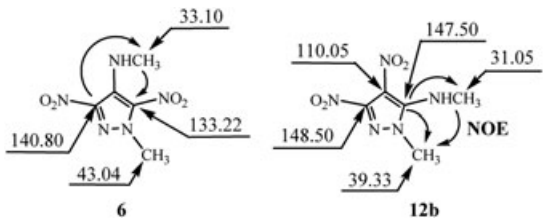


Figure 4

Table 1

Crystal data and structure refinement parameters for **1, 3c, 4**, and **NH_4-5a**.

	1	**3c**	**NH_4-5a**	**4**
Empirical formula	$C_3HN_5O_6$	$C_5H_5N_9O_6$	$C_6H_{14}N_{12}O_9$	$C_4H_3N_5O_6$
Formula weight	203.09	287.18	398.29	217.11
T (K)	100	100	100	100
Crystal system	Monoclinic	Orthorhombic	Triclinic	Orthorhombic
Space group	$P2_1/c$	$P2_{111}$	P-1	$Pna2_1$
Z	12	4	2	4
a (Å)	15.0080 (5)	5.11410 (10)	7.71350 (10)	11.7333 (3)
b (Å)	8.1732 (3)	11.5978 (2)	8.11350 (10)	8.2594 (2)
c (Å)	17.1160 (5)	17.5197 (3)	13.6005 (2)	8.3398 (2)
α (°)	90.00	90.00	104.8350 (10)	90.00
β (°)	92.2510 (10)	90.00	95.5290 (10)	90.00
γ (°)	90.00	90.00	108.8760 (11)	90.00
V (Å^3)	2097.89 (12)	1039.13 (3)	763.461 (18)	808.21 (3)
D_{calc} (g cm^{-3})	1.929	1.836	1.733	1.784
Linear absorption, μ (cm^{-1})	1.88	1.66	1.59	1.69
F(000)	1224	584	412	440
$2\theta_{max}$ (°)	60	60	60	59
Reflections measured	99,797	46,209	50,284	37,641
Independent reflections	6120	1777	4444	1252
Observed reflections [with $I > 2\sigma(I)$]	5500	1728	4186	1249
Parameters	391	201	304	149
R1	0.0330	0.0239	0.0300	0.0219
wR2	0.0957	0.0665	0.0940	0.0602
GOF	1.007	1.001	1.008	1.005
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.524/–0.335	0.360/–0.206	0.465/–0.321	0.279/–0.178

Our results show the inversion of reactivity of TNP on going from neutral heterocycle to its anion: the "electrophilic" position becomes "nucleophilic."

CONCLUSIONS

This work shows that fully C-nitrated pyrazole—TNP—possesses the intriguing properties which distinguish it from its congeners: its N-anion undergoes the nucleophilic substitution of 4-nitro group under mild conditions while its covalent derivative—MTNP—behaves in completely different way; here, the same nucleophiles substitute only 5-nitro group. The data obtained in this work clearly show that TNP is a novel, multipurpose building block in the pyrazole family. The future applications of this novel tecton will open unprecedented perspectives in the design of new polyfunctional pyrazoles.

EXPERIMENTAL

Melting points were determined on a Reichert Kofler thermopan apparatus and were uncorrected. NMR spectra were recorded in DMSO-d_6 solutions (unless otherwise is stated) at 298 K on a "Bruker AC-300" [operating at 300.13 MHz (^{1}H), 75.47 (^{13}C)] and "Bruker DRX-500" [operating at 500.13 MHz (^{1}H), 125.77 (^{13}C)] spectrometer. Tetramethylsilane was used as an internal standard for ^{1}H and ^{13}C, and CH_3NO_2 was used as an internal standard for ^{14}N, high-field chemical shifts are given with the minus sign. IR spectra were measured on a Bruker ALPHA spectrometer in KBr pellets and UV spectra were recorded on a Specord UV VIS instrument. Mass spectra were obtained on a FINNIGAN MAT INCOS 50 and Bruker MicrOTOF II instruments. Elemental analysis was performed with a Perkin-Elmer Series II 2400 analyzer. The course of the reactions was monitored and the purity of the compounds was checked by TLC on Merck Silicagel 60 F_{254} plates.

X-Ray diffraction experiments. XRD experiments for **1**, **3c**, **4**, and **NH_4-5a** were carried out with a Bruker's SMART APEX2 CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scans]. The structures were solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. Hydrogen atoms were located from the Fourier synthesis of the electron density and refined in the isotropic approximation. Crystal data and structure refinement parameters for **1**, **3c**, **4**, and **NH_4-5a** are summarized in Table 1. All calculations were performed using SHELXTL PLUS 5.0. [33].

The calculated density of the compounds **1** and MTNP **4** at RT is 1.876 and 1.726 g cm^{-3}, respectively. Note that despite the failure to obtain the correct space group for **1** [23], the crystal densities theoretically predicted for TNP **1** and MNTP **4** reproduce those obtained from XRD data with ~7% error.

3,4,5-Trinitro-1H-pyrazole (1). A solution of **2** [16] (18.6 g, 0.12 mol) in a mixture of H_2SO_4 (d = 1.824 g cm^{-3}, 186 mL) and HNO_3 (d = 1.51 g cm^{-3}, 75 mL) was kept at 90–100°C for 10 h. The resulting mixture was poured into ice-water (1 L), and extracted with ethyl acetate (2 × 300 mL). The organic layer was separated, washed with water, and dried over $MgSO_4$. The solvent was then removed *in vacuo*, and the residue was crystallized from toluene. Yield: 20.7 g (87%) **1**; mp 186°C (ref. 9; mp 187.8°C, ref. 10; mp 182–184°C).

Synthesis of 3,4,5-trinitro-1H-pyrazole salts 3a-c (general procedure). To the solution of trinitropyrazole **1** (0.5 mol) in

MeOH (3 mL) was added ammonia (25% solution in water, 1 equiv) or KOAc (1 equiv) or *N*-amino-1,2,4-triazole (1 equiv) in MeOH (3 mL). The mixture was stirred for 4 h at room temperature. The solvent was then removed *in vacuo*, the residue was washed with ether and dried over P_2O_5 in cases **3a** and **3b**. In the case of **3c**, the precipitate formed was filtered off, washed with ether, and dried over P_2O_5.

3,4,5-Trinitro-1H-pyrazole ammonium salt (3a). Yield 89%; mp 195–198°C; ^{13}C-NMR: δ 122.06 (C4), 146.90 (C3,5). Anal. Calcd. for $C_3H_4N_6O_6$: C, 16.37; H, 1.83; N, 38.18. Found: C, 16.52; H, 1.90; N, 40.11.

3,4,5-Trinitro-1H-pyrazole potassium salt (3b). Yield 95%; mp 199–201°C; ^{13}C-NMR: δ 122.03 (C4), 147.24 (C3,5). Anal. Calcd. for $C_3KN_5O_6$: C, 14.94; K, 16.21; N, 29.04. Found: C, 15.14; K, 16.36; N, 29.63.

3,4,5-Trinitro-1H-pyrazole N-amino-1,2,4-triazolium solt (3c). Yield 90%, mp 165°C. ^{13}C-NMR: δ 122.06 (C4), 143.97, 146.91 (C3,5). Anal. Calcd. for $C_5H_5N_9O_6$: C, 20.91; H, 1.76; N, 43.90. Found: C, 21.23; H, 1.88; N, 44.60.

Synthesis of 1-methyl-3,4,5-trinitro-1H-pyrazole (4) and 1-methyl-4-methylamino-3,5-dinitro-1H-pyrazole (6) (general procedure). To the solution of $NaHCO_3$ (0.51 g, 6 mmol) in water (10 mL), compounds **1** or **5b** (3 mmol) were added. The mixture was stirred for 10 min, followed by addition of Me_2SO_4 (0.34 mL, 3.6 mmol). The stirring was continued for 4 h at room temperature. The precipitate formed was filtered off and dried over P_2O_5.

4. Yield 92%; mp 90–91°C ($CHCl_3$) (ref. 12; mp 91.3°C); IR: 1587, 1540, 1338 (NO_2) cm^{-1}; ^{1}H-NMR (($CD_3)_2CO$): δ 4.50 (s, 3H); ^{13}C-NMR (($CD_3)_2CO$): δ 43.86, 124.22 (C4), 139.70 (C5), 143.20 (C3); ^{14}N-NMR (($CD_3)_2CO$): δ −31.23 (C3NO_2), −32.70 (C5NO_2), −35.51 (C4NO_2), −76.25 (N2), −182.79 (N1); HRMS ESI(−): *m/z* 187.0119 Calc. for $(M\text{-}NO)^{-\cdot}$ 187.0109. Anal. Calcd. for $C_4H_3N_5O_6$: C, 22.13; H, 1.39; N, 32.26. Found: C, 22.28; H, 1.56; N, 32.57.

6. Yield 90%; mp 130–131°C (CH_2Cl_2); IR: 3365, 3326, (NH); 1615; 1527, 1479, 1438, 1333, 1306 (NO_2) cm^{-1}; ^{1}H-NMR: δ 2.95 (d, 3H, ^3J = 5.3 Hz), 4.16 (s, 3H), 7.26 (br d, 1H, ^3J = 4.9 Hz); ^{13}C-NMR: δ 33.10, 43.04, 130.87 (C4), 133.22 (C5), 140.80 (C3); ms: *m/z* 201 $(M)^+$. Anal. Calcd. for $C_5H_7N_5O_4$: C, 29.86; H, 3.51; N, 34.82. Found: C, 30.25; H, 3.71; N, 35.44.

Synthesis of 4-NR′R″-3,5-dinitro-1H-pyrazole 5a–h (general procedure). To the solution of trinitropyrazole **1** (0.5 g, 2.5mmol) in water (5 mL), the appropriate amine (10 equiv in the case of **5a**,**b** and 3.5 equiv in the case of **5c**–**h**) was added and the reaction mixture was left for 10 h at room temperature. The precipitate was filtered off, washed with cold MeOH, suspended in 3 mL of water, and acidified with 20% H_2SO_4 to pH 1. The resulting precipitate was filtered off, dried, and crystallized from EtOH-H_2O (1:1).

4-Amino-3,5-dinitro-1H-pyrazole (5a). Yield 80%; mp 166–168°C (ref. 27; mp 169–171°C); uv: (H_2O): λ max 260 nm (ε12,000), λ max 400 nm (ε 9,600); (aq. NaOH): λ max 306 nm (ε 16,200), λ max 400 nm (ε 8,400); (aq. H_2SO_4): λ max 222 nm (ε 12,400); pKa = 3.42, pK_{BH+} = −5.43; IR: 3436, 3324, 3172 (NH); 1650, 1525, 1350 (NO_2) cm^{-1}; ^{13}C-NMR: δ 128.96 (C4), 138.84 (C3,5); ^{14}N-NMR (($CD_3)_2CO$): δ −25.15 ($\nu_{1/2}$ 80 Hz, NO_2); HRMS ESI(−): *m/z* 172.0117 $(M\text{-}H)^-$. Calc. for $C_3H_2N_5O_4^-$ 172.0112.

4-Methylamino-3,5-dinitro-1H-pyrazole (5b). Yield 87%; mp 170–171°C; IR: 3360, 3144 (NH), 1620, 1488, 1424, 1388, 1352, 1304 (NO_2) cm^{-1}; ^{1}H-NMR: δ 3.00 (c, 3H); ^{13}C-NMR: δ 33.31 (CH_3), 129.83 (C4), 139.39 (C3,5); ms: *m/z* 187 $(M)^+$. Anal. Calcd. for $C_4H_5N_5O_4$: C, 25.68; H, 2.69; N, 37.43. Found: C, 25.90; H, 2.81; N, 37.84.

3,5-Dinitro-4-(pyrrolidin-1-yl)-1H-pyrazole (5c). Yield 80%; mp 170–172°C; IR: 3330, 2944 (NH), 1612, 1420, 1366, 1304, (NO_2) cm^{-1}; ^{1}H-NMR: δ 1.92 (m, 4H), 3.36 (m, 4H); ^{13}C-NMR: δ 25.44, 51.92, 125.17 (C4), 141.39 (C3,5); ms: *m/z* 227 $(M)^+$. Anal. Calcd. for $C_7H_9N_5O_4$: C, 37.01; H, 3.99; N, 30.83. Found: C, 37.19; H, 4.05; N, 31.16.

4-(3,5-Dinitro-1H-pyrazole-4-yl)morpholine (5d). Yield 74%; T. decomp. 238°C; IR: 3024, 2972 (NH), 1604, 1500, 1456, 1392, 1368 (NO_2) cm^{-1}; ^{1}H-NMR: δ 3.22 (m, 4H), 3.75 (m, 4H); ^{13}C-NMR: δ 50.79, 66.43, 126.22 (C4), 143.50 (C3,5); ms: *m/z* 243 $(M)^+$. Anal. Calcd. for $C_7H_9N_5O_5$: C, 34.57; H, 3.73; N, 28.80. Found: C, 34.74; H, 3.97; N, 29.02.

1-(3,5-Dinitro-1H-pyrazole-4-yl)azepane (5e). Yield 87%; mp 188–190°C; IR: 3022, 2980 (NH), 1600, 1556, 1480, 1392, 1336 (NO_2) cm^{-1}; ^{1}H-NMR: δ 1.65 (m, 8H), 3.24 (m, 4H); ^{13}C-NMR: δ 27.60, 29.00, 53.74, 128.14 (C4), 144.15 (C3,5); ms: *m/z* 255 $(M)^+$. Anal. Calcd. for $C_9H_{13}N_5O_4$: C, 42.35; H, 5.13; N, 27.44. Found: C, 42.49; H, 5.21; N, 27.68.

1-(3,5-Dinitro-1H-pyrazole-4-yl)piperidine (5f). 89%; mp 166–168°C; IR: 3232, 2932, 2848 (NH), 1600, 1404, 1304 (NO_2) cm^{-1}; ^{1}H-NMR: δ 1.61 (m, 6H), 3.12 (m, 4H); ^{13}C-NMR: δ 22.68, 25.94, 51.90, 127.60 (C4), 143.06 (C3,5); ms: *m/z* 241 $(M)^+$. Anal. Calcd. for $C_8H_{11}N_5O_4$: C, 39.84; H, 4.60; N, 29.04. Found: C, 40.06; H, 4.77; N, 29.40.

1-(3,5-Dinitro-1H-pyrazole-4-yl)-4-methylpiperidine (5g). Yield 74%; mp 138–139°C; IR: 3248, 2960, 2932 (NH), 1528, 1464, 1364, 1300 (NO_2) cm^{-1}; ^{1}H-NMR: δ 0.93 (d, 3H), 1.30 (m, 2H), 1.55 (m, 1H), 1.64 (m, 2H), 3.08 (m, 2H), 3.21 (m, 2H); ^{13}C-NMR: δ 21.14, 28.02, 30.22, 34.02, 43.29, 51.25, 127.51 (C4), 146.86 (C3,5); ms: *m/z* 255 $(M)^+$. Anal. Calcd. for $C_9H_{13}N_5O_4$: C, 42.35; H, 5.13; N, 27.44. Found: C, 42.47; H, 5.28; N, 27.65.

1-(3,5-Dinitro-1H-pyrazole-4-yl)-4-methylpiperazine (5h). Yield 84%; T. decomp. 247°C; IR: 2960, 2692 (NH), 1596, 1412, 1402, 1372, 1304, 1272 (NO_2) cm^{-1}; ^{1}H-NMR: δ 2.81 (s, 3H), 3.15 (m, 2H), 3.42 (m, 4H), 3.58 (m, 2H); ^{13}C-NMR: δ 40.33, 47.35, 52.85, 125.08 (C4), 144.99 (C3,5); ms: *m/z* 256 $(M)^+$. Anal. Calcd. for $C_8H_{12}N_6O_4$: C, 37.50; H, 4.72; N, 32.80. Found: C, 37.67; H, 4.71; N, 32.93.

Preparation of 4-amino-3,5-dinitro-1H-pyrazole 5a from carbamate 7. The solution of KOH (7.23g , 0.13 mol) and carbamate **7** [28] (10 g, 0.043 mol) in H_2O (100 mL) was heated at 80–90°C for 7 h. The resulting mixture was cooled down and left overnight. The precipitate of potassium salt was filtered off, washed with ice-water, suspended in water, and acidified by 20% H_2SO_4 to pH 1. The resulting precipitate was filtered off and dried over P_2O_5.

Yield 5 g (67%); mp 166–168°C (H_2O) (ref. 27; mp 169–171°C).

Synthesis of 3,5-dinitro-4-OR-1H-pyrazoles 8a–f and 3,5-dinitro-4-SR-1H-pyrazoles 9a–f (general procedure). To the solution of trinitropyrazole **1** (0.61 g, 3 mmol) in water (10 mL), NaOH (0.24 g, 3 mmol) was added, and the mixture with stirred for 10 min, then solution of NaOH (3 mmol) and the appropriate phenol (or 2,2,2-trifluoroethanole) (3 mmol) or thiol (3.6 mmol) in water (10 mL) was added slowly. The stirring was continued for 10 h in the case of phenols and 3 h in the case of thiols at room temperature, then the mixture was acidified with 20% H_2SO_4 to pH 1. The precipitate formed was filtered off, dried, and crystallized from MeOH-H_2O. In the case of **8d**, the resulting mixture was extracted with ethyl acetate (2 × 10 mL). The organic layer was separated and dried over $MgSO_4$. The solvent was then removed *in vacuo*, and the residue was washed with hexane.

3,5-Dinitro-4-phenoxy-1H-pyrazole (8a). Yield 50%; mp 162–164°C; IR: 3492, 3260 (NH), 1620, 1564, 1436, 1372, 1300 (NO_2) cm^{-1}; ^{1}H-NMR: δ 7.07 (m, 3H), 7.32 (m, 2H). ^{13}C-NMR: δ 115.19 (CH), 123.26 (CH), 127.77 (C4), 129.79 (CH), 143.49 (C3,5), 156.73 (CO); ms: *m/z* 250 $(M)^+$. Anal. Calcd. for $C_9H_9N_4O_5$: C, 43.21; H, 2.42; N, 22.40. Found: C, 43.60; H, 2.59; N, 22.73.

4-(2-Methoxyphenoxy)-3,5-dinitro-1H-pyrazole (8b). Yield 88%; mp 144–145°C; IR: 3490, 3488 (NH), 1556, 1512, 1372, 1336 (NO_2) cm^{-1}; ^{1}H-NMR: δ 3.81 (s, 3H, Me), 6.80 (m, 1H), 6.88 (m, 1H), 7.03 (m, 1H), 7.13 (m, 1H). ^{13}C-NMR: δ 55.95, 113.29 (CH), 115.07 (CH), 120.60 (CH), 124.19 (CH), 128.68 (C4), 142.84 (C3,5), 145.76, 148.69 (C O); ms: *m/z* 280 $(M)^+$. Anal. Calcd. for $C_{10}H_8N_4O_6$: C, 42.87; H, 2.88; N, 20.00. Found: C, 43.04; H, 2.95; N, 20.32.

4-(4-Chlorophenoxy)-3,5-dinitro-1H-pyrazole (8c). Yield 75%; mp 129–131°C; IR: 3574, 2992 (NH), 1596, 1512, 1402, 1310 (NO_2) cm^{-1}; ^{1}H-NMR: δ 7.09 (d, 2H), 7.38 (d, 2H); ^{13}C-NMR: δ 117.20 (CH), 127.24, 127.46 (C4), 129.62 (CH), 143.47 (C3,5), 155.58 (C O); ms: *m/z* 284, 286 (2:3) $(M)^+$. Anal. Calcd. for $C_9H_5ClN_4O_5$ C, 37.98; H, 1.77; N, 19.69. Found: C, 38.33; H, 1.94; N, 19.78.

4-(3,4-Dimethylphenoxy)-3,5-dinitro-1H-pyrazole (8d). Yield 67%; mp 206–208°C; IR: 3580, 2992 (NH), 1560, 1488, 1368, 1336 (NO_2) cm^{-1}; ^{1}H-NMR: δ 2.15 (s, 6H, Me), 6.76 (m, 1H), 6.83 (m, 1H), 7.03 (m, 1H); ^{13}C-NMR: δ 18.46 (Me), 19.39 (Me), 112.24 (CH), 116.13 (CH), 128.11 (C4), 130.37 (CH), 131.17, 138.00, 143.07 (C3,5), 154.81 (C O); ms: *m/z* 278 $(M)^+$. Anal. Calcd. for $C_{11}H_{10}N_4O_5$: C, 47.49; H, 3.62; N, 20.14. Found: C, 47.85; H, 3.90; N, 20.41.

3,5-Dinitro-4-[3-(trifluoromethyl)phenoxy]-1H-pyrazole (8e). Yield 50%; mp 136–138°C; IR: 3628, 3490, 2992 (NH), 1596, 1512, 1480, 1316 (NO_2) cm^{-1}; ^{1}H-NMR: δ 7.38 (m, 1H), 7.45 (m, 2H), 7.57 (m, 1H); ^{13}C-NMR: δ 112.44 (CH), 119.62 (CH), 120.20 (CH), 123.80 (q, CF_3), 127.13 (C4), 131.30 (CH), 143.65 (C3,5), 157.05 (C O); ms: *m/z* 318 $(M)^+$. Anal. Calcd. for $C_{10}H_5F_3N_4O_5$: C, 37.75; H, 1.58; N, 17.61. Found: C, 38.02; H, 1.66; N, 17.78.

3,5-Dinitro-4-(2,2,2-trifluoroethoxy)-1H-pyrazole (8f). Yield 49%; mp 133–135°C; IR: 3674, 3490, (NH), 1596, 1560, 1478, 1334 (NO_2) cm^{-1}; ^{1}H-NMR: δ 4.83 (q, 2H); ^{13}C-NMR: δ 70.18 (q, CH_2), 121.32 (q, CF_3), 131.44 (C4), 142.85 (C3,5), 161.06 (C–O); ms: *m/z* 256 $(M)^+$. Anal. Calcd. for $C_5H_3F_3N_4O_5$: C, 23.45; H, 1.18; N, 21.88. Found: C, 23.62; H, 1.30; N, 22.17.

4-(Ethylthio)-3,5-dinitro-1H-pyrazole (9a). Yield 70%; mp 92–93°C; IR: 3544, 3428 (NH), 1556, 1512, 1480, 1400, 1348, 1320 (NO_2) cm^{-1}; ^{1}H-NMR: δ 1.15 (t, 3H), 2.95 (q, 2H); ^{13}C-NMR: δ 14.45, 28.85, 107.54 (C4), 151.62 (C3,5); ms: *m/z* 218 $(M)^+$. Anal. Calcd. for $C_5H_6N_4O_4S$: C, 27.52; H, 2.75; N, 25.68. Found: C, 27.97; H, 2.92; N, 26.04.

3,5-Dinitro-4-(phenylthio)-1H-pyrazole (9b). Yield 98%; mp 155–156°C; IR: 3540, 3428 (NH), 1556, 1512, 1440, 1376, 1320 (NO_2) cm^{-1}; ^{1}H-NMR: δ 7.35 (m, 5H); ^{13}C-NMR: δ 105.13 (C4), 127.05, 128.15, 129.33, 133.82, 151.58 (C3,5); ms: *m/z* 266 $(M)^+$. Anal. Calcd. for $C_9H_6N_4O_4S$: C, 40.60; H, 2.26; N, 21.05. Found: C, 40.84; H, 2.38; N, 21.22.

4-[(4-Bromophenyl)thio]-3,5-dinitro-1H-pyrazole (9c). Yield 91%; mp 136–137°C; IR: 3588, 3088 (NH), 1552, 1472, 1404, 1388, 1316 (NO_2) cm^{-1}; ^{1}H-NMR: δ 7.17 (d, 2H), 7.45 (d, 2H); ^{13}C-NMR: δ 103.81 (C4), 119.80, 129.83, 132.02, 133.92, 152.10 (C3,5); ms: *m/z* 344, 346 (1:1) $(M)^+$. Anal. Calcd. for $C_9H_5BrN_4O_4S$: C, 31.32; H, 1.46; N, 16.23. Found: C, 31.58; H, 1.55; N, 16.36.

4-[(4-Chlorophenyl)thio]-3,5-dinitro-1H-pyrazole (9d). Yield 85%; mp 138–139°C; IR: 3580, 3088 (NH), 1552, 1480, 1472, 1388, 1316 (NO_2) cm^{-1}; ^{1}H-NMR: δ 7.15 (d, 2H), 7.45 (d, 2H); ^{13}C-NMR: δ 103.88 (C4), 119.88, 129.90, 132.02, 133.81, 151.91 (C3,5). Anal. Calcd. for $C_9H_5ClN_4O_4S$: C, 35.94; H, 1.68; N, 18.63. Found: C, 36.41; H, 1.80; N, 18.83.

4-[(4-Chlorobenzyl)thio]-3,5-dinitro-1H-pyrazole (9e). Yield 95%; mp 166–167°C; IR: 2968, 2924 (NH), 1560, 1488, 1472, 1396, 1312 (NO_2) cm^{-1}; ^{1}H-NMR: δ 4.23 (s, 2H), 7.15 (d, 2H), 7.39 (d, 2H); ^{13}C-NMR: δ 38.19, 105.77 (C4), 128.40, 130.68, 131.15, 136.00, 152.32 (C3,5); ms: *m/z* 314, 316 (3:2) $(M)^+$. Anal. Calcd. for $C_{10}H_7ClN_4O_4S$: C, 38.16; H, 2.24; N, 17.80. Found: C, 38.55; H, 2.30; N, 17.92.

S-(3,5-Dinitro-1H-pyrazole-4-yl) hydrogen thiocarbonate (9f). Yield 78%; mp 114–115°C; IR: 1712, 1680 (COOH), 1560, 1408, 1396, 1324, 1316 (NO_2) cm^{-1}; ^{1}H-NMR: δ 3.72 (s, 2H); ^{13}C-NMR: δ 36.13, 106.30 (C4), 151.90 (C3,5), 170.34; ms: *m/z* 246 $(M–2H)^+$. Anal. Calcd. for $C_5H_4N_4O_6S$: C, 24.20; H, 1.62; N, 22.58. Found: C, 24.42; H, 1.90; N, 22.77.

4-Hydroxy-3,5-dinitro-1H-pyrazole disodium salt (10). To the solution of $NaHCO_3$ (1.05 g, 12.5 mmol) in water (5 mL), trinitropyrazole **1** (0.5 g, 2.5 mmol) was added. The mixture was heated at 80–90°C for 9 h. After cooling, EtOH (5 mL) was added and the resulting mixture was kept at 0–5°C for 2 h. The precipitate formed was filtered off, washed with EtOH, and dried *in vacuo* over P_2O_5. Yield 0.15 g (28%); IR: 1556, 1488, 1348, 1320 (NO_2) cm^{-1}; ^{13}C-NMR: δ 145.08 (C4), 154.15 (C3,5); HRMS ESI(–) $C_3N_4O_5^{2-}$ Na_2^+ *m/z*: 172.9956. Calc. for $C_3HN_4O_5^-$ $[M - 2Na + H]^-$ 172.9952. Anal. Calcd. for $C_3N_4Na_2O_5$: C, 16.53; N, 25.70, Na, 21.09. Found: C, 16.70; N, 25.96, Na, 21.33.

Synthesis of 4-(*N*-azolyl)-3,5-dinitropyrazoles 11a–f (general procedure). A solution of trinitropyrazole **1** (3 mmol), NH-azole (3 mmol), and NaOH (6 mmol) in water (10 mL) was stirred at 80–90°C for 9 h. After cooling, the mixture was acidified with 20% H_2SO_4 to reach pH 1. The precipitate formed was filtered off, washed with cool water, and dried *in vacuo* over P_2O_5. Recrystallization from EtOH-H_2O (1:1) gave analytically pure samples.

3,5-Dinitro-4-(4-nitro-1H-pyrazol-1-yl)-1H-pyrazole (11a). Yield 61%; mp 215–216°C; IR: 3138 (NH), 1625, 1536, 1515, 1417, 1325 (NO_2) cm^{-1}; ^{1}H-NMR: δ 8.45 (s, 1H), 9.24 (s, 1H); ^{13}C-NMR: δ 110.66 (C4), 133.77 (CH), 135.92 (C4′NO_2), 136.69 (CH), 149.52 (C3,5); HRMS ESI(–): *m/z* 268.0064 $(M–H)^-$. Calc. for $C_6H_2N_7O_6^-$ 268.0072.

3,5-Dinitro-4-(3-nitro-1H-pyrazol-1-yl)-1H-pyrazole (11b). Yield 52%; T. decomp. 290°C; IR: 3162, 3139 (NH), 1557, 1389, 1342 (NO_2) cm^{-1}; ^{1}H-NMR: δ 7.23 (s, 1H), 8.31 (s, 1H); ^{13}C-NMR: δ 103.78 (CH), 110.78 (C4), 137.64 (CH), 149.45 (C3,5), 156.55 (C3′NO_2); ^{14}N-NMR ($(CD_3)_2CO$): δ –76.27 (br N2), –24.72, –21.62, (NO_2); HRMS ESI(–): *m/z* 268.0060 $(M-H)^-$. Calc. for $C_6H_2N_7O_6^-$ 268.0072.

3,5-Dinitro-4-(4-methyl-3-nitro-1H-pyrazol-1-yl)-1H-pyrazole (11c). Yield 63%; mp 150–151°C; IR: 3578, 3333 (NH), 1629, 1551, 1528, 1351, 1333 (NO_2) cm^{-1}; ^{1}H-NMR: δ 2.31 (s, 3H, Me), 8.12 (s, 1H). ^{13}C-NMR: δ 9.39 (Me), 110.94 (C4), 114.28 (C4′), 136.31 (CH), 148.95 (C3,5), 154.56 (C3′NO_2; HRMS ESI (–): *m/z* 282.0207 $(M - H)^-$. Calc. for $C_7H_4N_7O_6^-$ 282.0218.

3,5-Dinitro-4-(4-chloro-3-nitro-1H-pyrazol-1-yl)-1H-pyrazole (11d). Yield 80%; mp 135–136°C; IR: 3573, 3422 (NH), 1562, 1545, 1507, 1337 (NO_2), 837 (CCl) cm^{-1}; ^{1}H-NMR: δ 8.73

(s, 1H); ^{13}C-NMR: δ 105.97 (C4′Cl), 110.21 (C4), 135.57 (CH), 149.31 (C3,5), 151.11 (C3′NO_2); HRMS ESI(−): *m/z* 301.9678, 303.9648 (3 :1) $(M-H)^-$. Calc. for $C_6HClN_7O_7^-$ 301.9671, 303.9643.

4-(2-Methyl-4-nitro-1H-imidazol-1-yl)-3,5-dinitro-1H-pyrazole (11e). Yield 71%; mp 230–232°C; IR: 3162 (NH), 1627, 1506, 1379 (NO_2), 1102 cm^{-1}; ^{1}H-NMR: δ 2.35 (s, 3H, Me), 8.20 (s, 1H); ^{13}C-NMR: δ 13.68 (Me), 118.97 (CH), 123.75 (C4), 144.73 (C2′Me), 146.70 (C3,5), C4′NO_2 signals were not observer; HRMS ESI(−):*m/z* 268.0227 $(M-H)^-$. Calc. for $C_7H_4N_7O_6^-$ 268.0218.

3,5-Dinitro-4-(1H-1,2,4-triazol-1yl)-1H-pyrazole (11f). Yield 89%; mp 245–247°C; IR: 3456, 3138 (NH); 1624, 1533, 1448, 1333 (NO_2) cm^{-1}; ^{1}H-NMR: δ 8.20 (s, 1H), 8.82 (s, 1H); ^{13}C-NMR: δ 142.71 (C4), 144.57 (CH), 148.62 (C3,5), 151.86 (CH); ^{14}N-NMR ($(CD_3)_2CO$): δ −140.73 (br N1), −71.21 (br N2), −29.80, −24.55 (NO_2); HRMS ESI(−): *m/z* 226.0325 $(M-H)^-$. Calc. for $C_5H_2N_7O_4^-$ 226.0319.

Synthesis of 1-methyl-3,4-dinitro-5-NR′R″-1H-pyrazoles 12 and 13 (general procedure). To the solution of pyrazole **4** (2.0 mmol) in MeOH (10 mL), the 4 mmol of appropriate amine (or 10 mmol NH_3 and $MeNH_2$ in the case of **12a**,**b** as 24 and 40% solutions in water, respectively) was added, and the reaction mixture was left for 2 h in the case of amines and 48 h in the case of azoles at room temperature. The resulting mixture was kept at 0–5°C, the precipitate formed was filtered off, dried *in vacuo* over P_2O_5 and crystallized from MeOH-H_2O.

5-Amino-1-methyl-3,4-dinitro-1H-pyrazole (12a). Yield 70%; mp 122–123°C; IR: 3431, 3354, 3331 (NH), 1648; 1515, 1363 (NO_2) cm^{-1}; ^{1}H-NMR: δ 3.65 (s, 3H, NMe), 7.87 (br, 2H, NH_2); ^{13}C-NMR: δ 35.81 (NMe), 108.25 (C4), 146.95 (2C, C3, C5); ms: *m/z* 187 $(M)^+$. Anal. Calcd. for $C_4H_5N_5O_4$: C, 25.68; H, 2.69; N, 37.43. Found: C, 25.95; H, 2.84; N, 37.80.

1-Methyl-5-methylamino-3,4-dinitro-1H-pyrazole (12b). Yield 84%; mp 165–166°C; IR: 3350 (NH), 1629, 1542, 1454, 1331 (NO_2) cm^{-1}; ^{1}H-NMR: δ 3.15 (d, 3H, *J* = 5.4 Hz, $NHCH_3$), 3.85 (s, 3H, NMe), 7.65 (br q, 1H, *J* = 5.2 Hz, NHMe); ^{13}C-NMR: δ 31.05 (NHMe), 39.33 (NMe), 110.05 (C4), 147.50 (2C, C3, C5); ms: *m/z* 201 $(M)^+$. Anal. Calcd. for $C_5H_7N_5O_4$: C, 29.86; H, 3.51; N, 34.82. Found: C, 30.06; H, 3.68; N, 35.15.

1-Methyl-3,4-dinitro-5-(pyrrolidin-1-yl)-1H-pyrazole (12c). Yield 60%; mp 64–65°C; IR: 1586, 1547, 1451, 1396, 1323 (NO_2) cm^{-1}; ^{1}H-NMR: δ 1.96 (m, 4H), 3.50 (m, 4H), 3.86 (s, 3H, NMe); ^{13}C-NMR: δ 25.39, 39.49 (NMe), 50.48, 115.07 (C4), 145.28 (C5), 146.96 (C3); ms: *m/z* 241 $(M)^+$. Anal. Calcd. for $C_8H_{11}N_5O_4$: C, 39.84; H, 4.60; N, 29.04. Found: C, 40.12; H, 4.68; N, 29.38.

4-(1-Methyl-3,4-dinitro-1H-pyrazol-5-yl)morpholine (12d). Yield 64%; mp 92–93°C; IR: 1593, 1550, 1500, 1340 (NO_2), 1110 cm^{-1}; ^{1}H-NMR: δ 3.32 (m, 4H), 3.73 (m, 4H), 3.82 (s, 3H, NMe); ^{13}C-NMR: δ 37.61 (NMe), 49.27, 66.31, 118.18 (C4), 146.49 (C5), 146.77 (C3); ms: *m/z* 257 $(M)^+$. Anal. Calcd. for $C_8H_{11}N_5O_5$: C, 37.36; H, 4.31; N, 27.23. Found: C, 37.65; H, 4.46; N, 27.54.

1-(1-Methyl-3,4-dinitro-1H-pyrazol-5-yl)azepane (12e). Yield 61%; mp 65–66°C; IR: 1569, 1546, 1490, 1332 (NO_2) cm^{-1}; ^{1}H-NMR: δ 1.72 (m, 8H), 3.33 (m, 4H), 3.82 (s, 3H, NMe); ^{13}C-NMR: δ 27.18, 29.27, 37.15 (NMe), 52.61, 118.44 (C4), 146.62 (C3), 148.72 (C5); ms: *m/z* 269 $(M)^+$. Anal. Calcd. for $C_{10}H_{15}N_5O_4$: C, 44.61; H, 5.62; N, 26.01. Found: C, 44.93; H, 5.84; N, 26.30.

Ethyl 4-(1-methyl-3,4-dinitro-1H-pyrazol-5-yl)-piperazine-1-carboxylate (12f). Yield 82%; mp 123–124°C; IR: 1691 (COOR), 1582, 1498, 1432, 1251 (NO_2) cm^{-1}; ^{1}H-NMR: δ 1.20 (t, 3H, Me), 3.25 (m, 4H), 3.50 (m, 4H), 3.82 (s, 3H, NMe), 4.10 (q, 2H, CH_2); ^{13}C-NMR: δ 14.44, 37.62 (NMe), 43.70, 50.04, 60.93, 118.26 (C4), 146.64 (C5), 146.78 (C3), 154.57 (CO); ms: *m/z* 328 $(M)^+$. Anal. Calcd. for $C_{11}H_{16}N_6O_6$: C, 40.25; H, 4.91; N, 25.60. Found: C, 40.66; H, 5.05; N, 25.72.

5-(4-Fluorophenylamino)-1-methyl-3,4-dinitro-1H-pyrazole (12g). Yield 71%; mp 160–162°C; IR: 3335 (NH), 1595, 1510, 1491, 1371 (NO_2) cm^{-1}; ^{1}H-NMR: δ 3.59 (s, 3H, NMe), 7.15 (m, 4H), 9.50 (br, 1H, NH); ^{13}C-NMR: δ 38.07 (NMe), 115.05 (C4), 115.64 (CH), 121.12 (CH), 136.22, 141.95 (C5), 147.17 (C3), 158.35 (d, CF, *J* = 240 Hz); ms: *m/z* 281 $(M)^+$. Anal. Calcd. for $C_{10}H_8FN_5O_4$: C, 42.71; H, 2.87; N, 24.91. Found: C, 42.96; H, 3.04; N, 25.37.

5-(4-Chlorophenylamino)-1-methyl-3,4-dinitro-1H-pyrazole (12h). Yield 90%; mp 110–111°C; IR: 3342, 3325 (NH), 1601, 1579, 1492, 1242 (NO_2), 814 (Cl) cm^{-1}; ^{1}H-NMR: δ 3.67 (s, 3H, NMe), 7.02 (m, 2H), 7.32 (m, 2H), 9.60 (br, 1H, NH); ^{13}C-NMR: δ 37.87 (NMe), 119.72 (C4, CH), 126.40, 128.92 (CH), 139.31, 141.01 (C5), 147.12 (C3); ms: *m/z* 297, 299 (1:1) $(M)^+$. Anal. Calcd. for $C_{10}H_8ClN_5O_4$: C, 40.35; H, 2.71; N, 23.53. Found: C, 40.49; H, 2.84; N, 23.87.

1-Methyl-3,4-dinitro-5-(3-nitrophenylamino)-1H-pyrazole (12i). Yield 75%; mp 173–174°C; IR: 1577, 1524, 1497, 1350 (NO_2) cm^{-1}; ^{1}H-NMR: δ 3.72 (s, 3H, NMe), 7.34 (m, 1H), 7.56 (m, 1H), 7.85 (m, 2H), 10.0 (br, 1H, NH); ^{13}C-NMR: δ 37.76 (NMe), 111.60 (CH), 116.58 (CH), 117.12 (C4), 123.31 (CH), 130.40 (CH), 140.10 (C5), 142.12, 147.20 (C3), 148.41; ms: *m/z* 308 $(M)^+$. Anal. Calcd. for $C_{10}H_8N_6O_6$: C, 38.97; H, 2.62; N, 27.27. Found: C, 39.36; H, 2.70; N, 27.62.

3-[(1-Methyl-3,4-dinitro-1H-pyrazol-5-yl)amino]-1-propyl-1H-pyrazole (12j). Yield 60%; mp 120–121°C; IR: 3218, 2969 (NH), 1592, 1527, 1487, 1439, 1366 (NO_2) cm^{-1}; ^{1}H-NMR: δ 0.80 (t, 3H, Me), 1.72 (m, 2H, CH_2), 3.62 (s, 3H, NMe), 3.93 (q, 2H, CH_2), 6.00 (m, 1H), 7.65 (m, 1H), 9.65 (br, 1H, NH); ^{13}C-NMR: δ 10.69, 22.23, 38.15 (NMe), 52.84, 95.57 (CH), 113.82 (C4), 131.65 (CH), 141.98, 146.62 (C5, C3); ms: *m/z* 295 $(M)^+$. Anal. Calcd. for $C_{10}H_{13}N_7O_4$: C, 40.68; H, 4.44; N, 33.21. Found: C, 40.98; H, 4.60; N, 33.66.

1-Ethyl-N′-(1-methyl-3,4-dinitro-1H-pyrazol-5-yl)-1H-pyrazole-4-carbohydrazide (12k). Yield 90%; mp 225–226°C; IR: 3226, 2985 (NH), 1666 (CO), 1593, 1552, 1506, 1462, 1343, 1220 (NO_2) cm^{-1}; ^{1}H-NMR: δ 1.36 (t, 3H, Me), 3.76 (s, 3H, NMe), 4.21 (q, 2H, CH_2), 7.93 (s, 1H), 8.29 (s, 1H), 9.32 (br, 1H, NH), 10.64 (br, 1H, NH); ^{13}C-NMR: δ 15.22, 39.11 (NMe), 46.75, 111.68 (C4), 114.34, 131.47 (CH), 138.66 (CH), 146.77 (C5, C3), 162.42 (CO); ms: *m/z* 324 $(M)^+$. Anal. Calcd. for $C_{10}H_{12}N_8O_5$: C, 37.04; H, 3.73; N, 34.56. Found: C, 37.30; H, 3.88; N, 35.02.

1-Methyl-3,4-dinitro-5-(1H-pyrazol-1-yl)-1H-pyrazole (13a). Yield 76%; mp 104–105°C; IR: 1602, 1554, 1521, 1505, 1380, 1346 (NO_2) cm^{-1}; ^{1}H-NMR: δ 3.88 (s, 3H, NMe), 6.71 (m, 1H), 8.05 (m, 1H), 8.34 (m, 1H); ^{13}C-NMR: δ 38.61 (NMe), 108.79 (CH), 119.98 (C4), 134.65 (CH), 136.14 (C5), 144.24 (CH), 145.91 (C3); ms: *m/z* 238 $(M)^+$. Anal. Calcd. for $C_7H_6N_6O_4$: C, 35.30; H, 2.54; N, 35.29. Found: C, 35.47; H, 2.63; N, 35.82.

5-(Imidazol-1-yl)-1-methyl-3,4-dinitro-1H-pyrazole (13b). Yield 60%; mp 125–126°C; IR: 1556, 1488, 1368, 1316 (NO_2) cm^{-1}; ^{1}H-NMR: δ 3.80 (s, 3H, NMe), 7.23 (m, 1H), 7.63 (m, 1H), 8.15 (m, 1H); ^{13}C-NMR: δ 36.99 (NMe), 120.12 (C4), 120.91 (CH), 129.92 (CH), 134.68 (C5), 138.68 (CH), 146.36 (C3); ms: *m/z* 238 $(M)^+$. Anal. Calcd. for $C_7H_6N_6O_4$: C, 35.30; H, 2.54; N, 35.29. Found: C, 35.65; H, 2.70; N, 35.72.

1-Methyl-3,4-dinitro-5-(1,2,4-triazol-1-yl)-1H-pyrazole (13c). Yield 63%; mp 110–111°C; IR: 1595, 1539, 1510, 1351,

1279 (NO_2) cm^{-1}; ^{1}H-NMR: δ 3.91 (s, 3H, NMe), 8.62 (s, 1H), 9.23 (s, 1H); ^{13}C-NMR: δ 38.76 (NMe), 120.51 (C4), 133.30 (C5), 146.21 (C3), 148.44 (CH), 154.13 (CH); ms: *m/z* 239 $(M)^+$. Anal. Calcd. for $C_6H_5N_7O_4$: C, 30.13; H, 2.11; N, 41.00. Found: C, 30.28; H, 2.34; N, 41.56.

Synthesis of 1-methyl-3,4-dinitro-5-(nitropyrazolyl)-1H-pyrazoles 14 (general procedure). To the solution of NaOH (2 mmol) in water (3 mL), the appropriate nitropyrazole (2 mmol) was added, and the mixture with stirred for 10 min, then the solution of pyrazole **4** (2 mmol) in CH_3CN (10 mL) was added, and the reaction mixture was left for 1 h at ambient temperature. The solvent was then removed *in vacuo*, and the residue was extracted with $CHCl_3$ (3 × 5 mL). The organic layers were combined and dried over $MgSO_4$. The solvent was then removed *in vacuo*, and the residue was crystallized from petroleum-ether (**14a**) or chromatographed on silica (eluent $CHCl_3$, R_f 0.35) (**14b**).

1-Methyl-3,4-dinitro-5-(3-nitro-1H-pyrazol-1-yl)-1H-pyrazole (14a). Yield 92%; oil; IR: 1556, 1512, 1472, 1348, 1320 (NO_2) cm^{-1}; ^{1}H-NMR: δ 3.95 (s, 3H, NMe), 7.50 (m, 1H), 8.15 (m, 1H); ^{13}C-NMR: δ 38.64 (NMe), 104.86 (CH), 120.98 (C4), 134.40 (C5), 139.26 (CH), 146.05 (C3), 158.67 (C3′NO_2); ms: *m/z* 283 $(M)^+$. Anal. Calcd. for $C_7H_5N_7O_6$: C, 29.69; H, 1.78; N, 34.63. Found: C, 30.05; H, 2.02; N, 34.92.

1-Methyl-3,4-dinitro-5-(4-nitro-1H-pyrazol-1-yl)-1H-pyrazole (14b). Yield 71%; mp 108–109°C; IR: 1602, 1590, 1549, 1525, 1406, 1365, 1311 (NO_2) cm^{-1}; ^{1}H-NMR: δ 3.97 (s, 3H, NMe), 8.86 (s, 1H), 9.52 (s, 1H); ^{13}C-NMR: δ 38.67 (NMe), 120.09 (C4), 134.27 (C5), 135.36 (CH), 137.34 (C4′NO_2), 139.35 (CH), 146.04 (C3); ms: *m/z* 283 $(M)^+$. Anal. Calcd. for $C_7H_5N_7O_6$: C, 29.69; H, 1.78; N, 34.63. Found: C, 30.12; H, 1.93; N, 35.06.

Syntheses of 1-methyl-3,4-dinitro-5-OR-1H-pyrazoles 15a–e, 16a,b, 17 and 1-methyl-3,4-dinitro-5-SR-1H-pyrazoles 18a–d (general procedure). To the solution of NaOH (2 mmol) in water (3 mL), the appropriate phenol, oxime, propargyl alcohol, or thiol (2 mmol) was added, and the mixture was stirred for 10 min, then solution of pyrazole **4** (2 mmol) in CH_3CN (10 mL) was added (in the case of **15e**: 4 mmol NaOH and 4 mmol of pyrazoles **4**), and reaction mixture was left for 1 h in the case of phenols and oximes or for 15 min in the case of thiols at ambient temperature. The solvent was then removed *in vacuo*, and the residue was filtered off and washed with water. In the case of **15d**,**e**, the precipitates formed were filtered off. All compounds were crystallized from MeOH-H_2O.

5-(4-Bromophenoxy)-1-methyl-3,4-dinitro-1H-pyrazole (15a). Yield 82%; mp 118–120°C; IR: 1557, 1514, 1482, 1367, 1234 (NO_2) cm^{-1}; ^{1}H-NMR: δ 3.82 (s, 3H, NMe), 7.31 (d, 2H), 7.63 (d, 2H); ^{13}C-NMR: δ 36.35 (NMe), 115.08 (C4), 117.15 (CBr), 117.89 (CH), 132.58 (CH), 145.15 (C5), 145.83 (C3), 154.26 (CO); ms: *m/z* 342, 344 (1:1) $(M)^+$. Anal. Calcd. for $C_{10}H_7BrN_4O_5$: C, 35.01; H, 2.06; N, 16.33. Found: C, 35.25; H, 2.18; N, 16.52.

5-(3-Methoxyphenoxy)-1-methyl-3,4-dinitro-1H-pyrazole (15b). Yield 80%; mp 91–92°C; IR: 1616; 1560, 1520, 1492, 1434, 1338, 1227 (NO_2), 1129 cm^{-1}; ^{1}H-NMR: δ 3.73 (s, 3H, NMe), 3.81 (s, 3H, OMe), 6.84 (m, 3H), 7.37 (m, 1H); ^{13}C-NMR: δ 36.30 (NMe), 54.76 (OMe), 102.32 (CH), 107.66 (CH), 110.84 (CH), 115.19 (C4), 130.80 (CH), 145.37 (C5), 145.75 (C3), 155.89, 160.81. Anal. Calcd. for $C_{11}H_{10}N_4O_6$: C, 44.90; H, 3.43; N, 19.04. Found: C, 45.25; H, 3.60; N, 19.18.

1-Methyl-3,4-dinitro-5-(2-nitrophenoxy)-1H-pyrazole (15c). Yield 70%; mp 151–152°C; IR: 1611; 1595, 1558, 1517, 1376, 1347 (NO_2) cm^{-1}; ^{1}H-NMR: δ 3.95 (s, 3H, NMe), 7.51 (m, 1H), 7.62 (m, 1H), 7.76 (m, 1H), 8.21 (m, 1H); ^{13}C-NMR: δ 36.49 (NMe), 114.86 (C4), 117.88 (CH), 126.12 (2 CH), 135.41 (CH), 139.04, 144.46 (C5), 145.91 (C3), 146.98. Anal. Calcd. for $C_{10}H_7N_5O_7$: C, 38.85; H, 2.28; N, 22.65. Found: C, 39.28; H, 2.45; N, 22.86.

1-Methyl-3,4-dinitro-5-(3,5-dinitrophenoxy)-1H-pyrazole (15d). Yield 85%; mp 205–206°C; IR: 1625; 1552, 1519, 1368, 1350 (NO_2), 1248 cm^{-1}; ^{1}H-NMR: δ 3.90 (s, 3H, NMe), 8.67 (s, 2H), 8.71 (s, 1H); ^{13}C-NMR: δ 36.68 (NMe), 115.25 (C4), 115.31 (CH), 117.83 (2 CH), 144.05 (C5), 146.03 (C3), 148.97, 155.10; HRMS ESI(+): *m/z* 377.0088 $(M + Na)^+$, calc. for $C_{10}H_6N_6O_9 + Na^+$ 377.0088; *m/z* 372.0539 $(M + NH_4)^+$, calc. for $C_{10}H_6N_6O_9 + NH_4^+$ 372.0535.

5,5′-[1,4-Phenylenebis(oxy)]bis(1-methyl-3,4-dinitro-1H-pyrazole) (15e). Yield 84%; mp 230–232°C; IR: 1566, 1515, 1493, 1366, 1335 (NO_2), 1227, 1164 cm^{-1}; ^{1}H-NMR: δ 3.83 (s, 6H, NMe), 7.49 (s, 4H); ^{13}C-NMR: δ 36.41 (NMe), 114.95 (C4), 117.51 (4 CH), 145.53 (C5), 145.86 (C3), 151.87 (CO); HRMS ESI(+): *m/z* 473.0408 $(M + Na)^+$, calc. for $C_{14}H_{10}N_8O_{10} + Na^+$ 473.0412; *m/z* 468.0849 $(M + NH_4)^+$, calc. for $C_{14}H_{10}N_8O_{10} + NH_4^+$ 468.0858.

Acetone O-(1-methyl-3,4-dinitro-1H-pyrazol-5-yl)oxime (16a). Yield 82%; mp 90–92°C; IR: 1588, 1536, 1432, 1336 (NO_2) cm^{-1}; ^{1}H-NMR: δ 1.96 (s, 3H, CMe), 2.17 (s, 3H, CMe), 3.84 (s, 3H, NMe); ^{13}C-NMR ($CDCl_3$): δ 16.79, 20.95, 36.91 (NMe), 115.63 (C4), 145.80 (C5), 148.96 (C3), 165.57; ms: *m/z* 243 $(M)^+$. Anal. Calcd. for $C_7H_9N_5O_5$: C, 34.57; H, 3.73; N, 28.80. Found: C, 34.76; H, 3.81; N, 29.24.

1-Phenylethanone O-(1-methyl-3,4-dinitro-1H-pyrazol-5-yl) oxime (16b). Yield 86%; mp 135–136°C (decomp.); IR: 1591, 1541, 1432, 1337 (NO_2) cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 2.61 (s, 3H, CMe), 3.96 (s, 3H, NMe), 7.50 (m, 3H), 7.63 (m, 2H); ^{13}C-NMR ($CDCl_3$): δ 14.45, 37.09 (NMe), 113.65 (C4), 126.94 (CH), 129.06 (CH), 131.49 (CH), 132.97 (CH), 138.65 (C5), 148.85 (C3), 164.87; ms: *m/z* 305 $(M)^+$. Anal. Calcd. for $C_{12}H_{11}N_5O_5$: C, 47.22; H, 3.63; N, 22.94. Found: C, 47.36; H, 3.77; N, 23.52.

1-Methyl-3,4-dinitro-5-(prop-2-yn-1-yloxy)-1H-pyrazole (17). Yield 66%; mp 75–76°C; IR: 3286, 3271 (HC≡), 1558, 1512, 1377, 1338 (NO_2) cm^{-1}; ^{1}H-NMR: δ 3.71 (s, 3H, NMe), 3.95 (s, 1H), 5.23 (s, 2H); ^{13}C-NMR ($CDCl_3$): δ 36.31 (NMe), 64.21 (CH_2), 75.61 (–C≡), 79.98 (HC≡), 115.60 (C4), 146.82 (C3), 148.05 (C5); ms: *m/z* 226 $(M)^+$. Anal. Calcd. for $C_7H_6N_4O_6$: C, 37.18; H, 2.67; N, 24.77. Found: C, 37.34; H, 2.88; N, 25.03.

5-Ethylthio-1-methyl-3,4-dinitro-1H-pyrazole (18a). Yield 80%; mp 68–70°C; IR: 1556, 1472, 1348, 1326 (NO_2) cm^{-1}; ^{1}H-NMR: δ 1.22 (t, 3H, Me), 3.08 (q, 2H, CH_2), 4.05 (s, 3H, NMe); ^{13}C-NMR ($CDCl_3$): δ 15.19, 30.15, 38.89 (NMe), 129.85 (C4), 136.96 (C5), 146.14 (C3); ms: *m/z* 232 $(M)^+$. Anal. Calcd. for $C_6H_8N_4O_4S$: C, 31.03; H, 3.47; N, 24.13. Found: C, 31.15; H, 3.68; N, 24.30.

1-Methyl-3,4-dinitro-5-phenylthio-1H-pyrazole (18b). Yield 72%; mp 100–101°C; IR: 1546, 1527, 1488, 1355, 1327 (NO_2) cm^{-1}; ^{1}H-NMR: δ 3.95 (s, 3H, NMe), 7.42 (m, 5H, Ph); ^{13}C-NMR: δ 39.19 (NMe), 128.49 (CH, C4), 129.65 (CH), 130.21, 130.31 (C5), 146.72 (C3); ms: *m/z* 280 $(M)^+$. Anal. Calcd. for $C_{10}H_8N_4O_4S$: C, 42.86; H, 2.88; N, 19.99. Found: C, 43.15; H, 3.01; N, 20.37.

1-Methyl-5-(4-methylphenyl)thio-3,4-dinitro-1H-pyrazole (18c). Yield 95%; mp 103–104°C; IR: 1549, 1518, 1491, 1355, 1326 (NO_2) cm^{-1}; ^{1}H-NMR: δ 2.26 (s, 3H, Me), 3.90 (s, 3H, NMe), 7.21 (m, 2H), 7.36 (m, 2H); ^{13}C-NMR: δ 20.72, 38.94 (NMe), 129.98 (2C CH, C4), 134.24, 135.91, 137.91 (C5), 146.17 (C3); ms: *m/z* 294 $(M)^+$. Anal.

Calcd. for $C_{11}H_{10}N_4O_4S$: C, 44.89; H, 3.43; N, 19.04. Found: C, 45.11; H, 3.68; N, 19.40.

5-(4-Chlorobenzyl)thio-1-methyl-3,4-dinitro-1H-pyrazole (18d). Yield 90%; mp 80–82°C; IR: 1556, 1540, 1488, 1348, 1316 (NO_2) 837 (CCl) cm^{-1}; ^{1}H-NMR: δ 3.76 (s, 3H, NMe), 4.30 (s, 2H, CH_2), 7.25 (m, 2H), 7.38 (m, 2H); ^{13}C-NMR: δ 38.21 (NMe, CH_2), 128.97 (CH, C4), 130.87 (CH), 131.07, 135.25 (C5), 136.38, 145.96 (C3); ms: *m/z* 328, 330 (3:2) $(M)^+$. Anal. Calcd. for $C_{11}H_9ClN_4O_4S$: C, 40.19; H, 2.76; N, 17.04. Found: C, 40.56; H, 2.90; N, 17.22.

1-Methyl-3,5-diamino-4-nitro-1H-pyrazoles 19a,b (general procedure). A solution of pyrazoles **12b** or **12d** (2 mmol) and morpholine or methylamine (as 40% solution in water) (6 mmol) in MeOH (10 mL) was refluxed for 5 h. In the case of **19a**, the precipitate formed in the reaction mixture was filtered off. In the case of **19b**, the solvent was removed *in vacuo*, and the residue was crystallized.

1-Methyl-5-(N-methylamino)-3-(morpholine-4-yl)-4-nitro-1H-pyrazole (19a). Yield 50%; mp 185–186°C (CH_3CN); IR: 3325, 2969, 2952, 2858 (NH), 1629, 1561, 1530, 1455, 1434, 1410, 1326 (NO_2), 1161, 1110, 1038 cm^{-1}; ^{1}H-NMR: δ 3.07 (t, 4H, J 3.0 Hz), 3.13 (d, 3H, J 5.4 Hz, NHMe), 3.67 (t, 4H, J 4.3 Hz), 3.72 (s, 3H, NMe), 7.56 (d, 1H, J 5.2 Hz, NHMe); ^{13}C-NMR: δ 30.86 (NHMe), 38.08 (NMe), 49.41, 65.68, 111.16 (C4), 148.61 (C5), 151.06 (C3); ms: *m/z* 241 $(M)^+$. Anal. Calcd. for $C_9H_{15}N_5O_3$: C, 44.81; H, 6.27; N, 29.03. Found: C, 45.30; H, 6.35; N, 29.32.

1-Methyl-3-(N-methylamino)-5-(morpholine-4-yl)-4-nitro-1H-pyrazole (19b). Yield 83%; mp 108–110°C (hexane); IR: 3423, 2955, 2852 (NH); 1593, 1509, 1458, 1348 (NO_2) cm^{-1}; 1157, 1114; ^{1}H-NMR: δ 2.82 (d, 3H, J 5.2 Hz, NHMe), 3.12 (t, 4H, J 3.1 Hz), 3.60 (s, 3H, NMe), 3.75 (t, 4H, J 4.0 Hz), 6.50 (br, 1H, NHMe); ^{13}C-NMR: δ 28.50 (NHMe), 35.42 (NMe), 48.47, 66.43, 114.25 (C4), 144.75 (C5), 151.06 (C3); ms: *m/z* 241 $(M)^+$. Anal. Calcd. for $C_9H_{15}N_5O_3$: C, 44.81; H, 6.27; N, 29.03. Found: C, 45.21; H, 6.24; N, 29.44.

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[19] It should be mentioned that salts **3a** and **3c** were also obtained in the work by Shreeve [11].

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